CEMENT AND LIME MANUFACTURE

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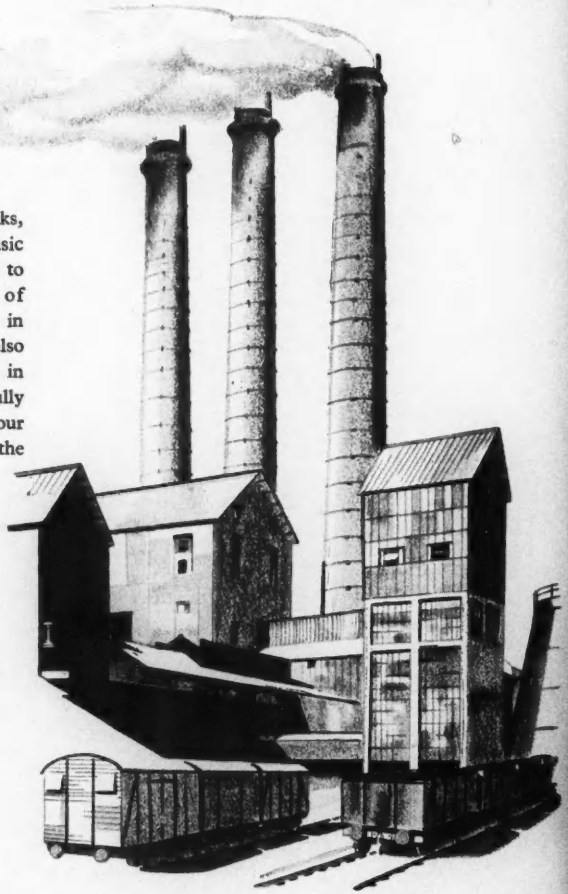

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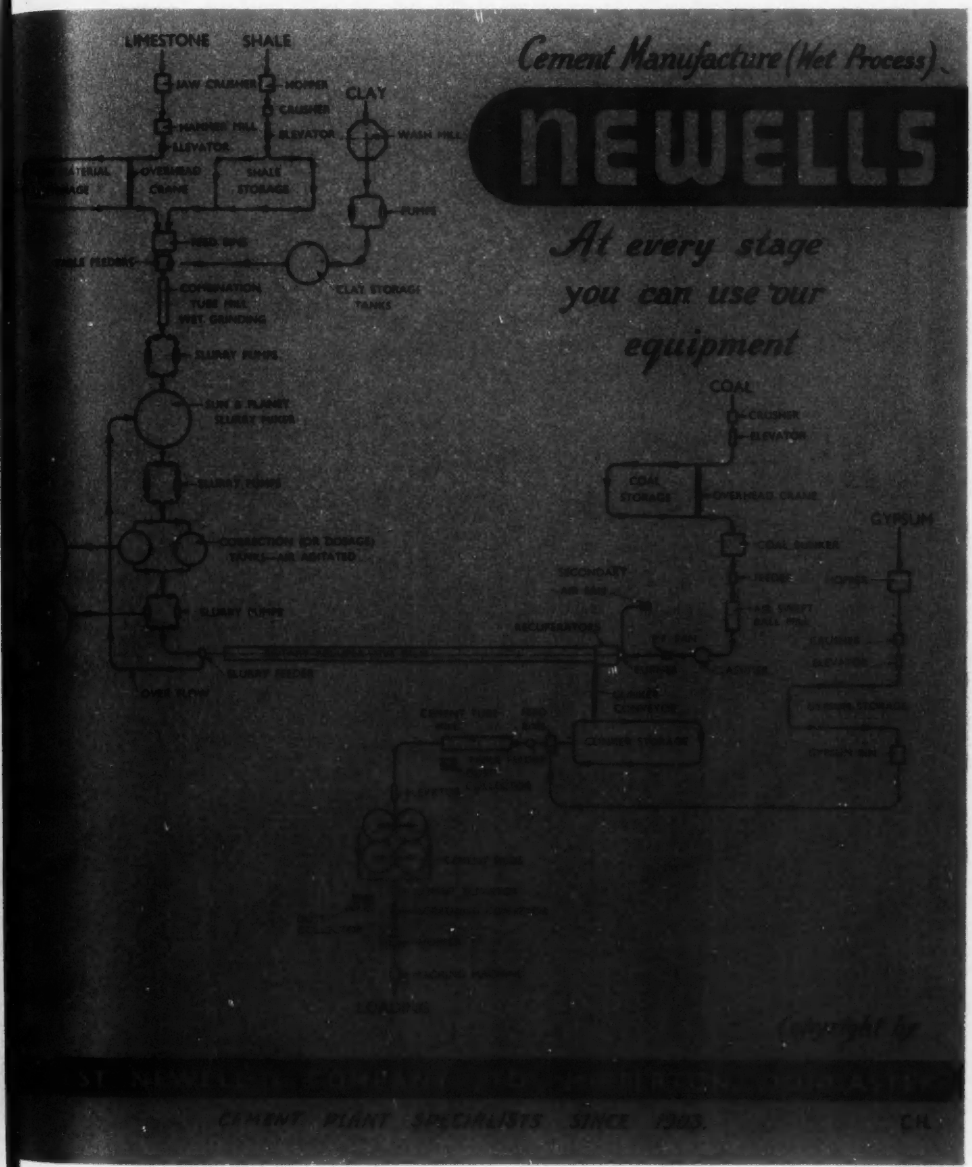
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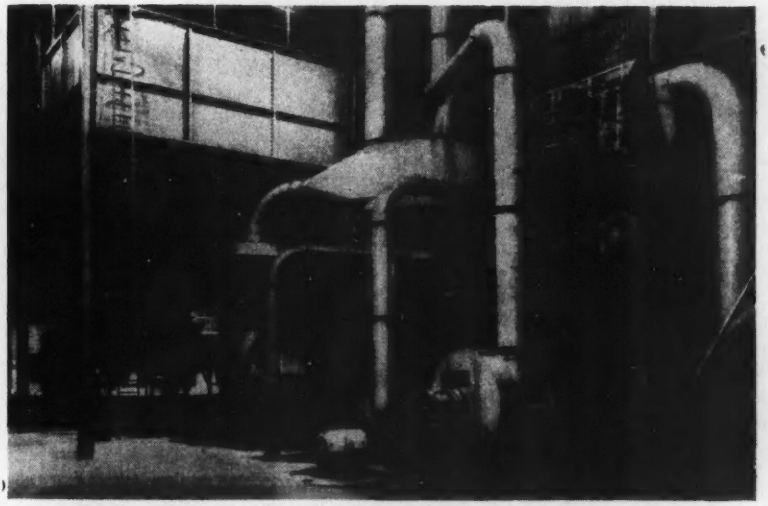

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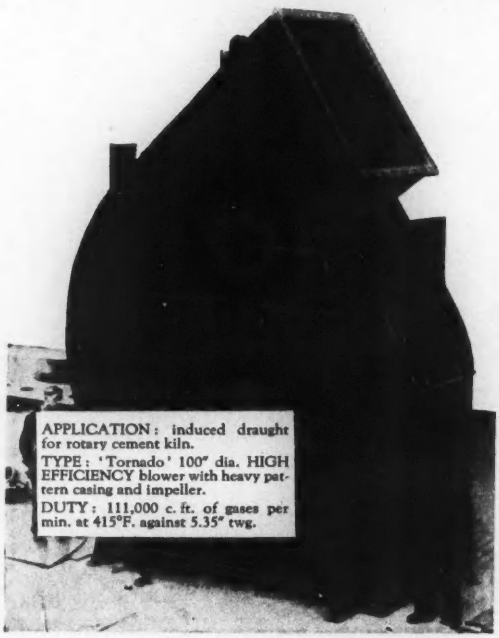

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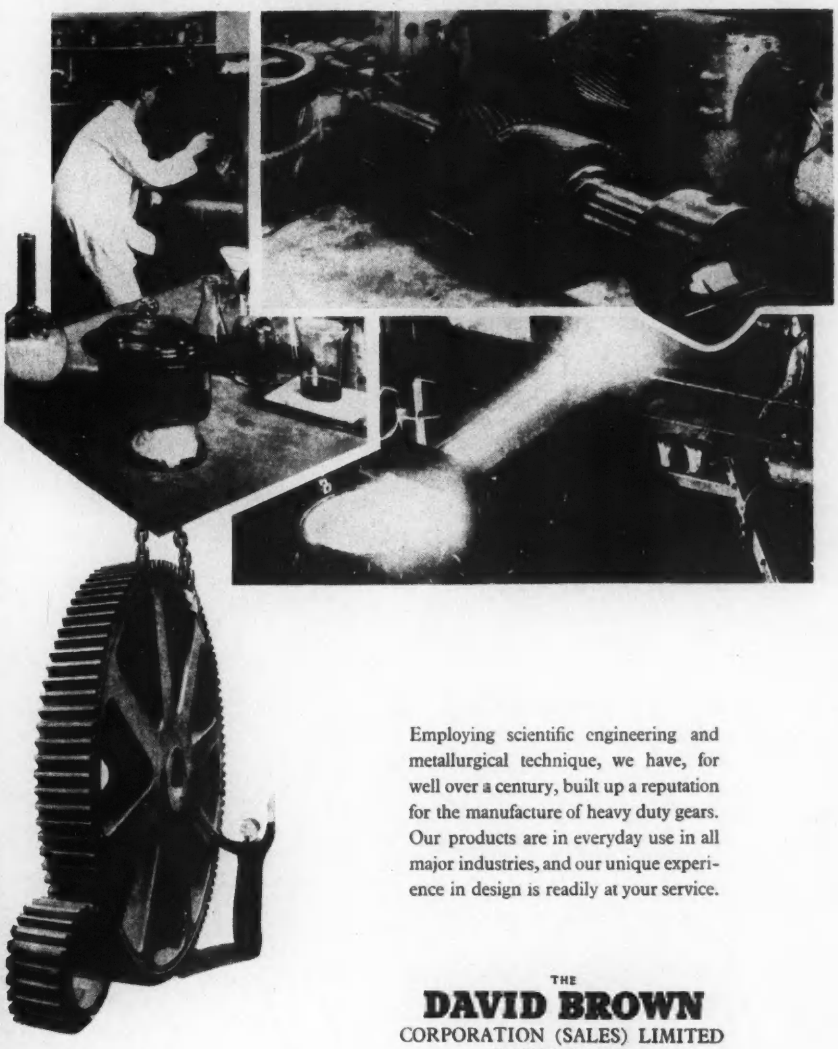

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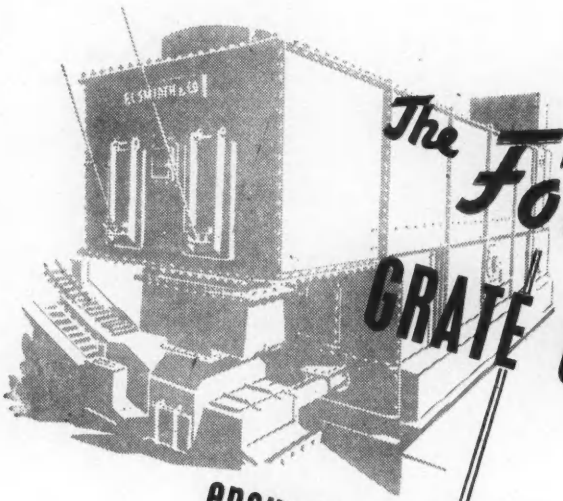

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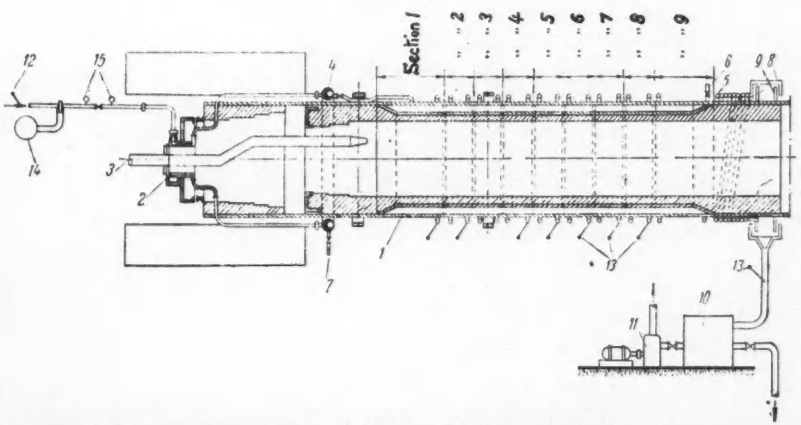
A Water-Cooled Kiln in Russia.

IN order to test its effectiveness in lengthening the useful life of kiln linings and improving thermal efficiency, a rotary kiln at a cement works at Gigant, Russia, has been fitted with a water-jacket to the design of M. N. I. Lukashin and M. N. P. Mel'nikov. Details of the first results of the test are given by M. K. S. Nekrasov in the Russian journal "Tsement."

The following is an abstract of this report.

The kiln is 353 ft. long by 11 ft. 9 in. diameter for 302 ft. and 11 ft. diameter for the remainder. The arrangement of the water-jacket is shown in *Fig.* 1. The jacket (1) is about 50 ft. long, one side being formed by the shell of the kiln and



1, Water jacket. 2, Stuffing-box. 3, Feed pipe. 4, Collector. 5, Water seals. 6, Air valve. 7, Discharge pipe. 8, Heater. 9, Flange. 10, Hot-water tank. 11, Pump. 12, 13, Thermometers. 14, 15, Manometers.

Fig. 1.—Arrangement of Water Jacket.

the other by a cylinder spaced about 4 in. from the kiln. To ensure more uniform application of cooling water to the shell, the jacket is divided by annular partitions into ten sections. A stuffing box (2) at the firing end of the kiln comprises a fixed part attached to the head of the kiln, and a rotating part attached to the kiln and arranged so that it can be adjusted to allow for any displacement of the kiln. Water pipes attached to the kiln are connected to the rotor by flexible rubber hose. The pipe carrying the coal fuel passes through the rotor.

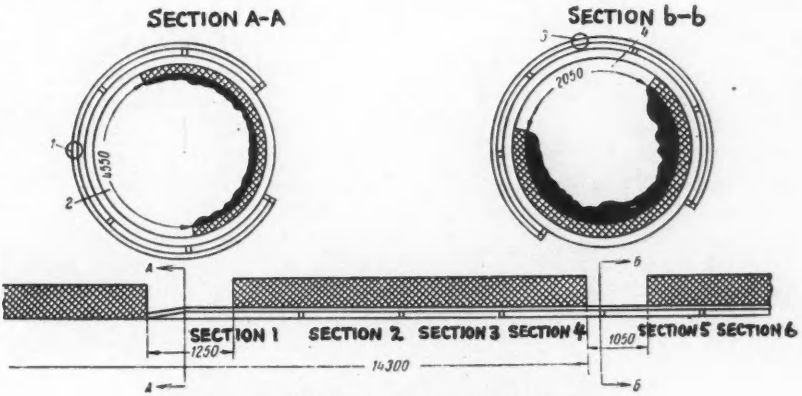
By means of pipes and a collector (4) attached to the kiln, cold water is supplied to each section and hot water removed thereform. The outlet ends of the pipes are fitted with an hydraulic seal or siphon (5). At section No. 10 of the jacket an air valve (6) is provided, whilst the collector near the first bearing is fitted with an outlet pipe (7) and valve. The ends of the water-discharge pipes are enclosed between two flanges (9) which are welded to the kiln and prevent the escape of water beyond the header (8) which is connected by a pipe with the hot-water tank (10). From this tank the water, at a temperature of 80 to 90 deg. C., is transferred by a centrifugal pump (11) to the wet mill where it is used for slurry mixing.

For measuring the temperature of the water in each section, nine resistance-thermometers are installed in the outlet pipes, and eighteen brass contact rings are mounted on the outside of the jacket. The temperatures are indicated on a panel on the head of the kiln. Resistance-thermometers Nos. 12 and 13 are also installed for measuring the temperatures of the cold and hot water, and the temperatures are automatically controlled at the head of the kiln. The amount of water supplied is determined by a differential manometer (14) and the pressure is measured by manometers at position 15.

The water-jacket was installed in February 1952, and the water was circulating at the rate of about 650 cu. ft. per hour when the kiln was fired. At the start, a zone of high temperature formed close to the end of the coal-firing jet, which hampered firing. This was rectified by reducing the supply of water to about 300 cu. ft. per hour and raising the temperature of the water to 85 to 90 deg. C. When the firing became normal the supply of water was again raised to about 650 cu. ft. per hour.

The lining of the kiln in the part that had been water-jacketted comprised chromo-magnesite bricks about 8 in. thick. A coating formed on the lining at this part and attained an appreciable thickness very quickly, and by reducing the supply of water and raising the temperature to 85 to 90 deg. C. formation of the coating of clinker was stabilised. The coating resembled the granular formation of clinker, and as well as a dense formation there was a more porous and friable structure with an uneven surface especially where the cold water entered the sections.

The first failures of the lining (*Fig.* 2) were in parts of sections Nos. 1, 4, and 5. These failures were due to the different expansions of the outer cylinder of the jacket and the shell of the kiln; the stresses thus produced exceeded the strength of the bricks and caused the lining to fail. *Table* 1 gives the results of the working



1, Water inlet of section 1. 2, Broken lining of section 1.
3, Water inlet for section 5. 4, Broken lining of section 5.

Fig. 2.—Condition of Lining at Time of Test.

of the kiln with and without the water-jacket. From these results the authors conclude that :

(1) The water jacket in the high temperature zone resulted in higher thermal intensity. Owing to the formation of the protective coating this rise in thermal intensity does not cause premature failure of the lining.

(2) The output increased despite the reduction of diameter in the sintering zone (from 10ft. 6in. to about 9ft. 9in. without counting the thickness of the coating). Further increase in performance is limited by the capacity of the preparatory zone.

(3) About 2·3 per cent. of fuel was saved, although the total requirement was 1992 cal/kg./kilolitre. The loss of heat in the exhaust gases was 442 deg. C., which is about 20 per cent. of the total heat used.

(4) Water-jacketing ensures the formation of a stable coating, attaining a

Table 1.—Results of Tests.

	Without jacket (August 1949)	With jacket (Feb. 1952)	With jacket (Oct. 1952)
Duration (hours)	24	24	47
Working of kiln (% of period) :			
At full load	94·4	87·5	87·0
At low load	5·6	12·5	8·2
Idle	—	—	4·8
Clinker output (cu. yd. per hour)	19	21	21·5
Specific consumption of burner fuel (kg./kg./kl.*)	0·428	0·360	0·398
Specific consumption of heat (cal./kg./kl.) ..	2002	1935	1992
Temperature of flue gas (deg. C.)	584	428	442
Heat intensity (cal/m.³/hr.)	330,000	515,000	540,000

* Kl=Kilolitre

maximum thickness of about 16 in. This protects the lining and shell from excessive overheating and failure.

(5) Tnis method of cooling does not lead to corrosion of the shell, and ensures better conditions for the workers.

(6) The system used at the Gigant works has some disadvantages which lower the coefficient of useful work. For example, the presence of two different cross sections of the kiln produces high stresses in the shell where the change of section occurs, attaining in parts 33,000 to 40,000 lb. per square inch. An increase in the temperature of the shell of the kiln by 50 deg. C. to 120 deg. C. results in an increase in stress of up to 80,000 lb. per square inch or more and this was no doubt the cause of the failure of the lining in these parts. The length of the water-jacket (about 50 ft.) was arrived at by calculations based on the full length of heating zone to ensure cooling of the material before it reached the sintering zone (sections 7, 8, 9), since in these sections the thickness of the coating is very thin (2 in. to 3 in.). This adversely affected the sintering zone and reduced efficiency. Also, the type of stuffing-gland used was unsatisfactory, and it is thought that omission of the enlarged ends of the jacket, reducing the length of the jacket to 33 ft., together with an improved type of stuffing-box, would ensure better heat conditions and longer life of the lining.

It is agreed that a water-jacket will lead to increased thermal efficiency and better protection of the refractory lining if the differences in the rate of expansion of the shell of the kiln can be avoided. It is suggested that this can be done by fixing the lining in separate panels with an expansion joint between the panels.

U.S.A. Specifications for Cement.

At a meeting held in January last of the committee of the American Society for Testing Materials some changes in the physical requirements for Portland cement in the Standard Specification for Portland cement (C.150) and in the Standard Specification for Air-entraining Portland cement (C.175) were accepted. The Committee recommends the deletion of the alternative test for strength related to the tensile strength of mortar briquettes and an increase in the present compressive strength requirements.

A new tentative method was accepted for the determination of the " false " set of Portland cement; this method makes use of a mechanical mixer and a modified Vicat apparatus using a brass rod with a stud on one end in place of the standard needle. Among the existing tentative methods approved for adoption as standards are the methods for determining heat of hydration (C.186), normal consistency (C.187), fineness by the use of the air-permeability apparatus (C.204 T), and the definition of the term " pozzolan " (C.219 T).

The System $CaO.Fe_2O_3$.

RESEARCH IN ITALY.

The results of an investigation on the system $CaO.Fe_2O_3$, carried out by B. Tarisci and G. Mulas, are described in the journal "La Chemica e L'Industria" (Milan). The investigations were conducted by microscopic observation, by reflection and with the use of X-rays. The results confirm the existence of the compound $CaO.Fe_2O_3$, which breaks down into Fe_2O_3 at a certain temperature and becomes a liquid mass. The following is an abstract of the paper.

This system has seldom been studied. By confining the investigation to the part rich in Fe_2O_3 the results obtained can be related to those of Sosman and Merwin[1] who did not find intermediate compounds between $CaO.Fe_2O_3$ and Fe_2O_3 and those of B. Tavasci[2] who, on the other hand, found $CaO.2Fe_2O_3$ which breaks down before melting at a temperature between 1,225 deg. C. and 1,230 deg. C. This compound corresponds to that found by the same author[3] in the system $CaO.Al_2O_3$. G. Malquori and V. Cirilli, in a paper at the Symposium on the Chemistry of Cement held at London in 1952, gave the results of their investigations, in which, although they noted contradictions between the results in the Sosman and Merwin diagram, they concluded that the latter was correct.

In the present investigation it was desired to repeat in part the researches of Malquori and Cirilli and in part those of B. Tavasci for the purpose of ascertaining the existence or otherwise of $CaO.2Fe_2O_3$. To avoid the risk of decomposition of Fe_2O_3 with liberation of oxygen, heating was conducted below 1,200 deg. C. so as to avoid a liquid phase. In order that the decomposition should be uniform, a 1 : 10 solution of hydrofluoric acid in a mixture of equal parts of alcohol and water was used as a reagent. The period of the attack was from 10 to 20 minutes. It was found that to obtain the necessary coloration of the constituent attacked the maximum period was necessary, whereas, to obtain one delimitation of the granules the minimum time sufficed.

The following are the results of the microscopic examinations. (The photographs have a magnification of 300.)

A mixture of $2CaO.3Fe_2O_3$ (corresponding to $CaO : Fe_2O_3 = 40 : 60$ examined by Malquori and Cirilli) was heated to a temperature of 1,160 deg. C. to 1,170 deg. C. and then placed for observation in styrol resin. When the preparation was polished for a short time it appeared to be a homogeneous mass. The use of the reagent showed the presence of two zones of which only one ($CaO.Fe_2O_3$) was not attacked. In *Fig.* 1 is seen a clear zone and a dark grey zone in which are crystals of elongated shape ; the black patches represent cavities.

A mixture of $CaO.2Fe_2O_3$ was heated to 1,180 deg. C. to 1,190 deg. C. The product obtained is shown in *Fig.* 2, in which the dark zones represent cavities. The substance with a grey tint is almost wholly attacked by the reagent. Crystallization similar to the grey zone in *Fig.* 1 is also seen. The same product is

obviously concerned, which now represents almost the whole. The remaining part consists of clear unattacked zones of two different types, both in appearance and in hardness. The zones of one type are identical with those of *Fig.* 1 ($CaO.Fe_2O_3$) ; in *Fig.* 2 these are shown by arrows. The zones of the other type

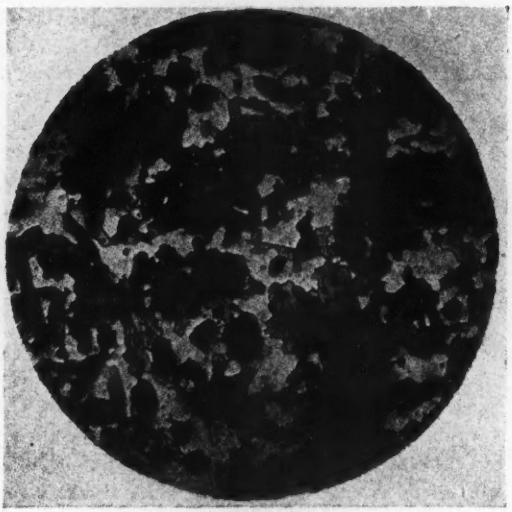


Fig. 1.

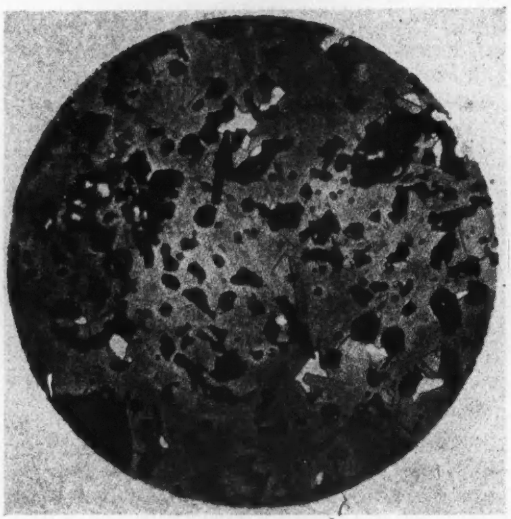


Fig. 2.

are out of focus due to very high relief, and are indicated by an arrow and a ring ; these zones are Fe_2O_3 which has not completely reacted. Bearing in mind that the total composition corresponds to $CaO.2Fe_2O_3$, and that opposite the zones of Fe_2O_3 there are zones of $CaO.Fe_2O_3$ (both in small quantities), it seems that the

Fig. 3.

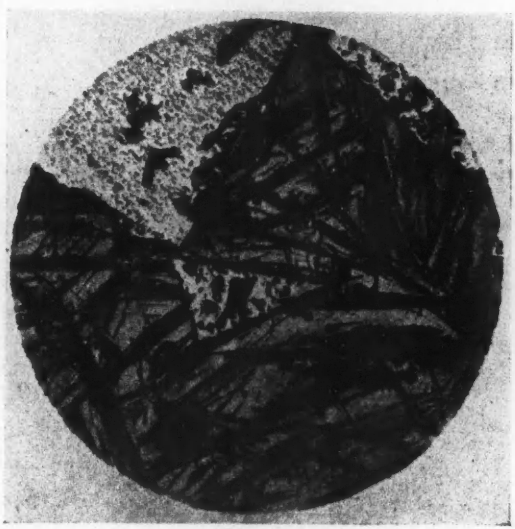


Fig. 4.

grey mass consists of $CaO.2Fe_2O_3$; this bears out the result previously obtained by B. Tavasci.[2]

A mixture of $CaO.3Fe_2O_3$ also heated to 1,780 deg. C to 1,790 deg. C. was found to be a mass that was not liable to attack in its entirety by the reagent, with minute granules in strong relief. The fundamental mass obviously consisted of $CaO.2Fe_2O_3$, and that in relief, in view of its proportions, must be Fe_2O_3. In *Fig.* 3 the black zones represent the pale granules of Fe_2O_3.

In the paper by Tavasci[2] it is stated that $CaO.2Fe_2O_3$ decomposes at 1,225 deg. C. to 1,230 deg. C. into Fe_2O_3 and a liquid mass; an attempt to determine the possible melting point has confirmed this. In the mass obtained there are seen (*Fig.* 4) large granules of Fe_2O_3 in high relief and imperfectly polished owing to their hardness (hæmatite is one of the most difficult minerals to polish); they

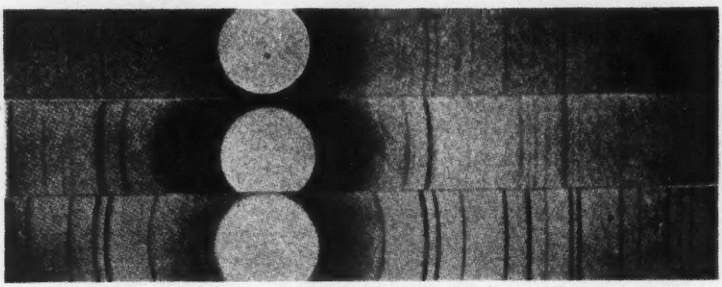
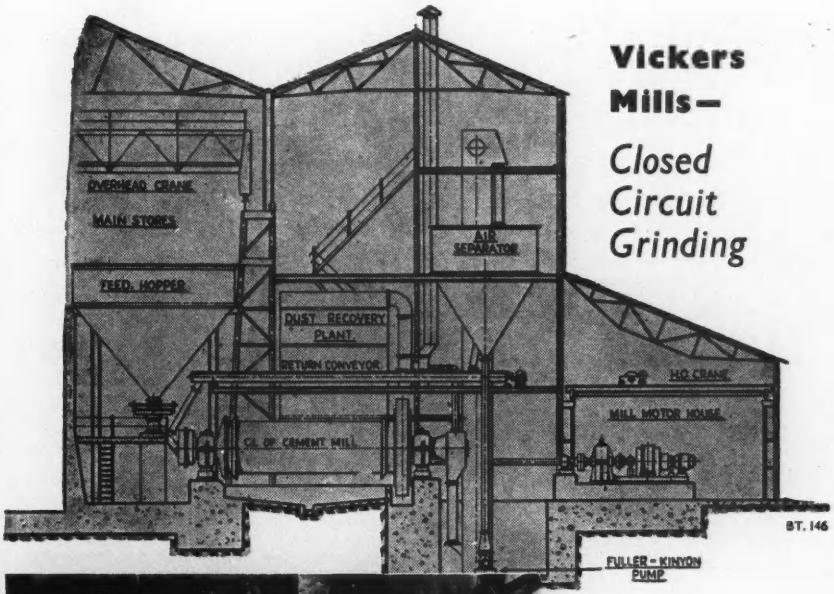


Fig. 5.—Top: $CaO.Fe_2O_3$. Middle: $CaO.2Fe_2O_3$. Bottom: Fe_2O_3.

are paler than the rest of the mass and are denoted by the letter F. The mass obtained by the solidification of the liquid consists of necessity of a mixture of $CaO.Fe_2O_3$ and $CaO.2Fe_2O_3$; the latter takes the form of large needles made dark by the reagent. By further polishing the two ferrites can also be distinguished by the greater hardness of $CaO.Fe_2O_3$ compared with $CaO.2Fe_2O_3$.

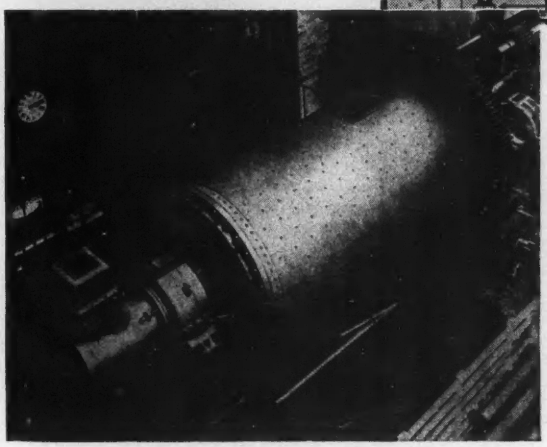
The X-ray tests were made primarily to ascertain the distinction between $CaO.Fe_2O_3$, $CaO.2Fe_2O_3$, and Fe_2O_3. A cobalt anticathode was used, and the film was placed according to Straumani's method. The X-ray photographs are reproduced in *Fig.* 5 (the part corresponding to the more diffracted rays, which is less clear, has been omitted). In the middle photograph the lines of $CaO.Fe_2O_3$ and Fe_2O_3 cannot be seen even if these substances were found microscopically (see *Fig.* 2); their presence is therefore less than can be seen with the aid of X-rays.

1 R. B. Sosman, H. E. Merwin, J. Wash, Acad. Science, 6, 532 (1916).
2 B. Tavasci, Ann. chim. applicata, 26, 291 (1936).
3 B. Tavasci, La Chimica e l'Ind. 17, 461 (1935).
4 G. Malquori, V. Cirilli. III. International Symposium on the Chemistry of Cement, London, 1952.



Vickers Mills—

Closed Circuit Grinding



Though a 'closed circuit' makes it easier to control production to a specific fineness, consistent accuracy depends upon the plant being reliable. The trouble-free running synonymous with Vickers mills demonstrates, in fact, that there is no substitute for skill and experience backed by manufacturing capacity.

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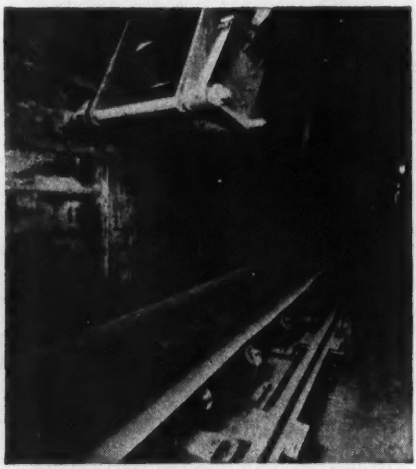

The ore unloading bench at Hawarden Bridge Steelworks. Ore dropped from rail waggons into the bunkers is loaded on to the Goodyear Conveyor Belt by an apron feeder car. Breakdowns here can't be tolerated, a good reason for fitting Goodyear.

Goodyear Conveyor Belting gives outstanding service in ore grading plant.

Here is another convincing example of the superiority of Goodyear Conveyor Belting.

Since its installation just over a year ago, a 60-inch Goodyear "Stacker" Conveyor Belt at the Hawarden Bridge Steelworks of John Summers and Sons Limited, has given typical Goodyear performance. The belt conveys iron ore and limestone, at the rate of 750 tons an hour, *and* is ready to take the increased load of greater output which is scheduled.

This is the first of a series of Goodyear belts installed for handling ore. Other Goodyear belts are in service in various parts of the works.

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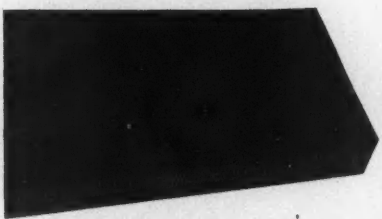

GOODYEAR

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Research on Lime.

As part of a series of investigations on the chemistry of lime, Mr. Gösta Ringqvist has attempted to supplement the existing data on the electrolytic conductivity of calcium hydroxide solutions with measurements within the temperature range 0 deg. to 100 deg. C. The results are given in tabular form in a brochure entitled " Condensation of Pure Calcium Hydroxide Solutions as a Function of Electrolytic Conductivity in the Temperature Range from 0 deg. to 100 deg. C.," issued by the Swedish Cement & Concrete Research Institute and printed in the English language. A calcium hydroxide solution of satisfactory purity was prepared as follows. Baker's grade *pa* pulverised calcium hydroxide was dissolved in hydrochloric acid 1 to 1. Ammonium oxalate was added, and calcium oxalate was precipitated by neutralising with ammonium hydroxide while boiling. All the chemicals used were of the purest grade. The precipitate was thoroughly washed in distilled water, dissolved in hydrochloric acid, precipitated again as oxalate, carefully washed, dried, and calcined in a platinum crucible in a muffle furnace. Distilled water was added to the pure calcium oxide obtained in this manner. The milk of lime was boiled and decanted twice. After that, the hydroxide was dried and calcined in a platinum crucible in a muffle furnace. Finally, the calcium oxide was dissolved in distilled water and transferred through a Jena G4 glass filter in atmosphere free from carbon dioxide to a polyethene flask in which it was stored.

The solution was analysed, first for the calcium ion content by precipitating the oxalate and by titrating it with potassium permanganate in a solution acidified with sulphuric acid, and secondly for the hydroxyl ion content by titrating with hydrochloric acid. The following average results were obtained from a large number of determinations. With potassium permanganate, $1{\cdot}216 \pm 0{\cdot}003$ grammes of CaO per litre of solution; with hydrochloric acid, $1{\cdot}218 \pm 0{\cdot}006$ grammes of CaO per litre of solution. The fact that both these analyses have given the same results shows that no foreign ions were present in the solution. The electrolytic conductivity of the solution must therefore be wholly attributed to the dissolved calcium hydroxide. For determinations to be made on solutions of lower concentration than the standard solution, this solution was diluted in a carbon-dioxide free atmosphere by means of a standard graduated flask. For determinations on solutions of higher concentration, the standard solution was evaporated and the concentration then determined by acid titration.

The measurements were made by means of a Philips GM 4249 conductivity bridge, and a Muirhead A-25-K decade group was used as a comparative resistance. The test cell was of the same type as Philips GM 4221, and was calibrated by comparison with N/50 and N/100 potassium chloride solutions. The same connecting wires with silver-coated contact pins were employed for calibrations and for measurements. The Pyrex glass test container was pretreated with boiling water; during the measurements, the container was kept at a constant temperature by means of circulating water controlled by a thermostat. The temperature of the solution was read on a precision thermometer fitted near the test cell in the test container. The solution was maintained at a constant temperature for

several hours. At the same time, the conductivity and the temperature were measured, and the test container was frequently shaken until complete temperature equilibrium was observed, so that no temperature variations exceeding 0·02 deg. C. were noticed during an interval of ten minutes.

The accuracy of the determination of the temperature of the test solution, inclusive of errors in readings, was $\pm$0·025 deg. C. This error did not affect even the third digit after the decimal point, and is therefore negligible. The conductivity bridge comprises compensating devices for capacitances which may occur in the test circuit. Furthermore, by calibrating two decade groups with respect to each other in the bridge circuit, it was found that the conductivity bridge did not give rise to any additional errors over and above those inherent in the decade groups, which amounted to $\pm$0·1 per cent. The accuracy in the calibration of the test cell was 0·2 ohm at a measured resistance of about 400 ohms. A calculation was made in order to determine the errors in measuring unknown resistances of calcium hydroxide solutions by the method described. At low conductivities these errors were found to be negligible. At the lowest resistances observed in these measurements, that is about 50 ohms, the error can be 0·2 ohm; this corresponds to a maximum error of 0·004 gramme of CaO per litre.

Cement Packed in a Ship.

The Skanska Cement Company of Sweden now has three ships specially converted for the transport of loose cement. The first, which was commissioned in 1948, has a capacity of 1,850 tons, and can transport about 500,000 tons a year to neighbouring ports. A year later another ship was converted to carrying loose cement, and this also soon became fully employed. It was decided that it was necessary to have one ship in reserve, and in order that it should not be idle a bagging plant was installed in the ship.

This ship has a capacity of 1,891 tons of loose cement and has a crew of 24 men. Silos for two types of cement are built into the largest hold. The cement is taken from the silos by chain conveyors to elevators which deliver it to a screw-conveyor on deck, which delivers the cement to a bagging plant on board or to equipment for discharging it loose. The two packing machines are in one of the holds, and the filled bags can be delivered through the side of the ship to vehicles on a quay. These ships are fully described in " Pit and Quarry " for November, 1954.

Proposed Cement Works in Indonesia.

Among new projects in Indonesia is a new cement works to be financed by the Government.

New Cement Works in Turkey.

The construction of five cement works in Turkey is to start this year.

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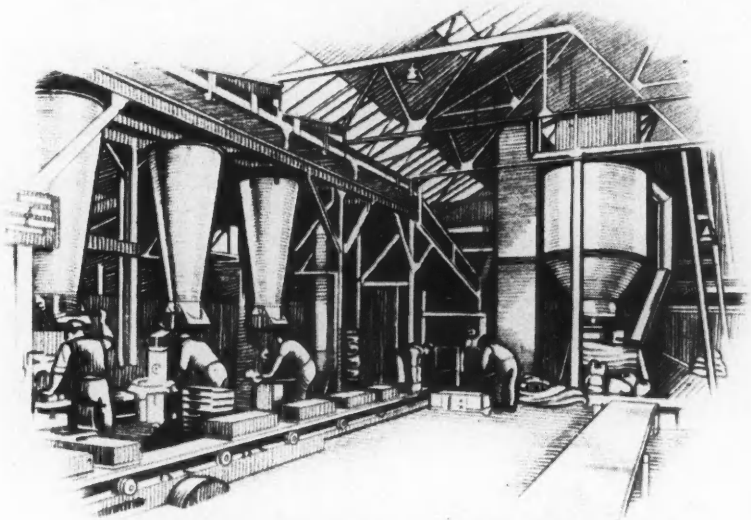

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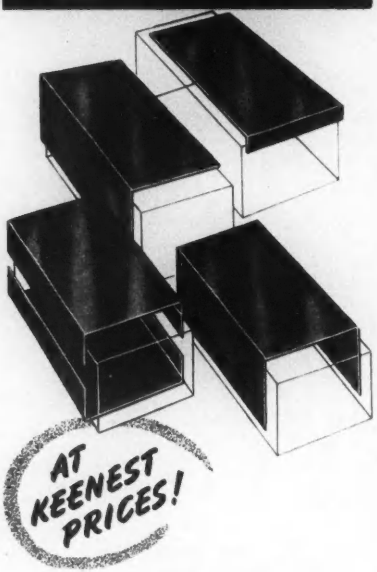

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Acid-resisting Concrete.

A NEW PROCESS.

A process for increasing the resistance of concrete to attack by acids has been produced by Ocratfabrik N.V., of Baarn, Holland, and is known as the "Ocrat" process. The purpose of the process is to treat concrete, after it has hardened, in such a way that the calcium compounds become insoluble in acids, and at the same time to make the concrete more dense and resistant to penetration by solutions.

The process employs the gas silicon tetrafluoride which is capable of penetrating deeply into concrete, where the following reaction occurs: $2\ Ca(OH)_2 + SiF_4 = 2CaF_2 + Si(OH)_4$. The lime portion is converted to insoluble calcium fluoride and the silica portion to silicic acid gel. When the calcium silicates and aluminates in cement react with water they form new water-containing compounds in which Ca- and -OH groups always occur. These also combine with the gas as in the equation.

Concrete products to be treated are allowed to harden and then dried and put into a pressure chamber which is evacuated, and silicon tetrafluoride gas is introduced. The depth of penetration, and hence of the protective layer, can be controlled by varying the pressure and time. In this way hydrated silica and alumina are deposited in the inner capillaries, increasing the density of the concrete, preventing penetration of aggressive solutions, and increasing the strength. In the case of thin sections the concrete can be treated throughout its depth.

The gas generator consists of a lead-lined container with a stirrer. The reaction is $2Na_2SiF_6 + SiO_2 + 2H_2SO_4 = 2NA_2SO_4 + 2H_2O + 3SiF_4$ or, if fluorspar is used, $2CaF_2 + SiO_2 + 2H_2SO_4 = 2CaSO_4 + 2H_2O + 3SiF_4$; the former is rather more economical.

An excess of sulphuric acid must be present at a temperature of 60 to 70 deg. C. The most effective form of silica is kieselguhr. The ground materials are stirred with sulphuric acid in the generator, which has a steam-jacket for heating the mixture. Gas is given off at once. The acid residue can be neutralized with lime. Before starting the process the gas generator and the chamber are evacuated, and the requisite quantity of sulphuric acid is drawn in by the vacuum.

Silicon tetrafluoride is 3·7 times as dense as air. It is colourless and attacks the mucous membrane, so that gas masks and rubber clothing are required when using it. The gas reacts rapidly with water: $3SiF_4 + 2H_2O = 2H_2SiF_4 + SiO_2$ (hydrate). The silicofluoric acid formed reacts with the concrete. Thus brief watering of the product frees it from traces of the gas.

The gas is allowed to flow from the generator to the chamber quickly at first then more slowly. By leaving it to stand overnight most of the gas is used up, or after four to six hours it can be blown out with air into an absorber containing sodium carbonate. The sodium silicofluoride formed in the absorber can be used in the generator. A block of treated concrete cut in two and immersed in

a 1:3 solution of hydrochloric acid had a hollow in the untreated central portion surrounded by a thick crust of the treated layer.

Before treatment, the concrete should have reached an age at which it has developed the greater part of its strength. This is normally at least two to three weeks with damp curing. Reinforcement is not attacked by the process. It has been found, even with a porous concrete, that a porcelain-like sheath is formed around the reinforcement and that this protects the steel during lengthy immersion in hydrochloric and lactic acids.

Cement Works Extension in Norway.

The Nordland Cement Company's works at Kjöpsnes is being extended to increase the annual production from 75,000 tons to about 135,000 tons. The cost is estimated to be 11½ million kronen, part of which is being supplied by the North of Norway Development Fund.

Cement Works for Korea.

The United Nations Reconstruction Office for Korea announces that Messrs. F. L. Smidth, of Copenhagen, have been commissioned to build a cement factory in South Korea. The annual capacity is to be 100,000 tons, and the cost is estimated to be 5,250,000 dollars.

Cement Production in Spain.

The total production of cement of all types in Spain was 3,308,000 tons in the year 1954; this is an increase of 19½ per cent. on the previous year.

A Tax on Cement in Italy.

The Italian Government has imposed a tax on cement made in that country. It is estimated that this tax will produce about 4 milliard lire a year (about £1,750,000 at the present rate of exchange).

Works Extension in Peru.

With a view to increasing the capacity of its works at Pacasmayo, in Northern Peru, the Compania de Cemento Portland del. Norte S.A. has decided to increase its capital by about one million pounds. Tenders for the plant have already been received. When the extension is completed the capacity of the works will be 100,000 tons a year.

Cement Production in Great Britain.

The production of cement in Great Britain averaged in 1954 a rate of a million tons a month for the first time. The total production exceeded that for 1953 by about 750,000 tons, an increase of rather more than 6½ per cent.

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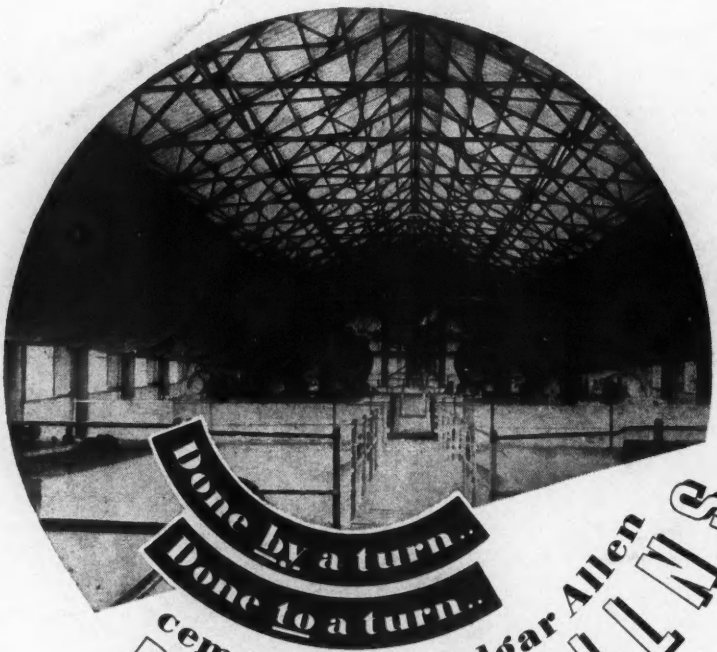

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